

MODELLING AND CONTROL OF THE MICROSTRUCTURE OF MAA-co-PEGMA WATER SOLUBLE COPOLYMERS

Iñaki Emaldi, POLYMAT and Kimika Aplikatua Saila, Kimika Zientzien Fakultatea, University of the Basque Country UPV/EHU, Joxe Mari Korta Zentroa, Spain
inaki.emaldi@ehu.eus

Shaghayegh Hamzehlou, POLYMAT and Kimika Aplikatua Saila, Kimika Zientzien Fakultatea, University of the Basque Country UPV/EHU, Joxe Mari Korta Zentroa, Spain

Amaia Agirre, POLYMAT and Kimika Aplikatua Saila, Kimika Zientzien Fakultatea, University of the Basque Country UPV/EHU, Joxe Mari Korta Zentroa, Spain

Eduarne Erkizia, Tecnalia Research & Innovation, Materials, Sustainable Construction Division, c/ Geldo, Spain
Jorge Sánchez Dolado, Concrete Modelling and Material Behaviour, Materials and Environment, The Netherlands ; Donostia International Physics Center (DIPC), Spain

Jose Ramon Leiza, POLYMAT and Kimika Aplikatua Saila, Kimika Zientzien Fakultatea, University of the Basque Country UPV/EHU, Joxe Mari Korta Zentroa, Spain

Key Words: Aqueous phase copolymerization; modelling and control; MAA; PEGMA; copolymer composition

Water soluble poly(MAA-co-PEGMA) copolymers present comb like structure, where the size of the lateral chain can be tuned by using PEGMA macromonomer of different number of ethylene glycol units. This type of macromolecules under alkali conditions present an anionic backbone due to the ionization of the carboxylic monomers, and uncharged side chains. This type of copolymers are widely used in construction as superplasticizers for cementitious formulations. It is known that several parameters such as the molar mass, lateral chain length and sequence distribution of the monomers in the chains have a tremendous impact on the performance of the copolymers when applied as superplasticizers. Therefore, obtaining copolymers with a controlled microstructure is required to be able to understand their interaction with the cementitious formulations.

Starved semibatch free radical copolymerization has been widely employed to control the chemical comonomer composition in both solution and emulsion polymerization. Despite of the good control on the composition, long addition times are required. Thus, the modelling of the addition policies is necessary in order to shorten the reaction times ensuring a homogenous composition and control of the molecular weight distribution through the whole reaction. The kinetics of the water soluble monomers are substantially more complex than non-water soluble ones, as their kinetics depend on various parameters such as monomer concentration, pH and ionic strength^{1, 2}. The knowledge of kinetics parameters and their dependency on different variable is the key parameter to develop a predictive mathematical model.

In the current work, a detailed mathematical model was developed to predict the microstructure of the copolymers considering all the complexities of the kinetics of water soluble monomers. Batch solution copolymerization reactions (using jacketed reactors and in situ NMR) and semibatch experiments were carried out with different feeding ratios at temperatures ranging from 70 to 90 °C and with the carboxylic monomer at fully ionized conditions. The kinetic parameters, namely reactivity ratios³ and propagation rate coefficients were estimated using experimental data of conversion, molecular weight as well as copolymer composition. Furthermore, the mathematical model was used to develop advance control strategies in a reaction calorimeter for the control of the microstructure of these copolymers.

1. Lacík, I.; Ucnová, L.; Kukučková, S.; Buback, M.; Hesse, P.; Beuermann, S. *Macromolecules*. 2009, 42, 7753-7761.
2. Smolne, S.; Weber, S.; Buback, M. *Macromol. Chem. Phys.* 2016, 217, 2391-2401.
3. Emaldi, I.; Hamzehlou, S.; Leiza, Dolado, J.S.; Leiza, J.R. *Processes*. 2017, 5, 19.